Available online at www.sciencedirect.com

ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry 188 (2007) 387–391

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

A comparative study of three techniques for determining photocatalytic activity

P. Evans [a,*], S. Mantke [a], A. Mills [b], A. Robinson [a], D.W. Sheel [a]

[a] Institute for Materials Research, Salford University, Salford, M5 4WT, United Kingdom
[b] Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, United Kingdom

Received 25 October 2006; received in revised form 21 December 2006; accepted 27 December 2006

Abstract

Quantitative measurement of the activity of photoactive films is an area of importance. The establishment of tests for standardisation of performance is important for efficient research but also a major milestone in achieving technology acceptance. In this paper, we compare three different techniques across a range of film samples from various sources. Furthermore, we demonstrate the potential of the dye-based approach as a quick and simple test. A series of photoactive film samples are compared for measured activity against each test. The test is shown to be capable of reproducible and quantitative activity results. The test has potential for use "in the field" for verification of in-use product activity.

Keywords: Photoactivity; Stearic acid; Dye test; Contact angle; TiO_2; Resazurin

1. Introduction

The ability of semiconductor photocatalysts, in particular titanium dioxide (TiO_2), to degrade a range of organic pollutants, offers many potential applications in areas, such as water and air purification and self-cleaning surfaces [1]. Indeed, commercial self-cleaning glass products are readily available worldwide produced by many of the World's leading glass manufacturers [2–4]. Fundamental to these products – due to its optical and electronic properties, chemical stability, and low cost – is a thin film (typically 15–20 nm) of crystalline anatase TiO_2 grown by chemical vapour deposition (CVD) [5].

The activity of photocatalytic TiO_2 films can vary considerably and is dependent on many factors, such as film thickness, substrate, roughness, crystallite size and deposition temperature, to name but a few. There are many different methods that can be used to determine the activity of photocatalytic surfaces. Popular techniques include those based on photo-oxidation of organic films (such as stearic acid [6]) or organic vapours [7] and contact angle changes [8]. Many of these methods require the use of complex apparatus being suitable only for use in the laboratory, and therefore cannot be adapted to a practical end use application.

There are, at present, a number of important initiatives set to address the issue of standardisation in semiconductor photocatalysis. For example, it is an important part of the newly founded, EU-funded 'Photocatalytic technologies and novel nanosurfaces materials' (PHONASUM) committee [9]. The International Organisation for Standardisation (ISO) [10] has also a committee working on fine ceramics (TC 206) that has recently published several photocatalyst test methods that are under development, originating from the Japanese Industrial Standards Committee (JISC), including ones for assessing their air-purification performance via the removal of NO_x (ISO/DIS22197-1) and the measurement of water droplet contact angle (ISO/WD 27448-1).

One exception to this could be a test based on the use of a dye. In this test, a change in the colour of a dye is used as an indicator of the photocatalytic activity of the surface [11]. While the use of dye-based activity has been reported previously, in almost all cases these tests are based upon the photo-oxidation of the dye. This in itself can be a very slow process, therefore giving limited suitable as a test in the field.

Recently, an alternative test based upon a colour change in a dye has been developed [12]. In brief, the formulation comprises: the redox dye, resazurin (Rz); a sacrificial electron donor,

---

* Corresponding author. Tel.: +44 1612954800.
E-mail address: p.evans@salford.ac.uk (P. Evans).

1010-6030/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2006.12.040

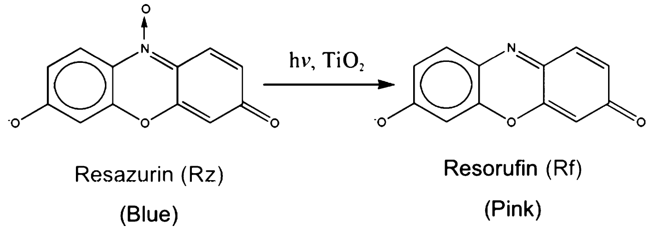

Fig. 1. A diagram to show the structures of the redox dye, resazurin (Rz) and in its reduced form, resorufin (Rf).

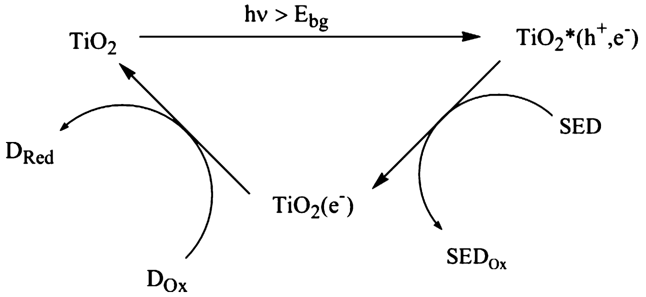

Fig. 2. A reaction scheme to the processes associated with the photoreduction of Rz on the surface of TiO_2 in the presence of ultra-bandgap light.

glycerol (SED); a polymer, hydroxy ethyl cellulose (HEC); dissolved in water. Whether wet or dry, upon irradiation of the ink on a photocatalytic surface with ultra-bandgap radiation, the photogenerated electrons reduce the blue Rz to the pink-resorufin (Rf) (Fig. 1), while the photogenerated holes oxidise the glycerol to glyceralaldehyde (Fig. 2). The process occurs rapidly making this test particularly suited to "on the spot" tests. In this paper, we show how this test can be used on photocatalytic TiO_2 surfaces, where the ink does not easily wet the surface, to assess the photoactivity of various TiO_2 CVD films. Furthermore, we compare this new photo-reductive dye method to the more widely reported techniques using stearic acid and changes in contact angle.

2. Experimental

2.1. Dye test

A previously reported formulation was used as the formulation for the work [12]. All chemicals were purchased from Sigma–Aldrich, and gases from BOC. For this, 10 mg of resazurin and 0.4 g of glycerol were mixed with 4 g of a 1.5 wt.% aqueous solution of hydroxyethyl cellulose. This solution was stirred for 30 min to ensure thorough dissolution of the ingredients. The dye formulation (two to three drops) was applied to the surface of the film sample (20 mm × 20 mm) using a pipette. A microscope slide (20 mm × 20 mm) was then placed onto the dye, causing the dye to spread evenly over the whole sample surface. The light absorption of the cover sheets was small enough (∼4%) to allow them to remain in place for the duration of the test. The samples were irradiated at 4 mW cm^{-2} with 365 nm BLB lamps. All UV–vis spectra were obtained using a Hewlett Packard 8452A diode array UV/vis spectrophotometer.

2.2. Stearic acid

The photocatalytic activities of the titanium dioxide films were also measured by studying the rate of degradation of stearic acid upon exposure to UV radiation. A layer of stearic acid was applied to the sample (typically 20 mm × 20 mm) using a 100 μL aliquot of a 10 mmol solution of stearic acid in methanol, and then immediately spun for 2 min at 2500 rpm. The integrated area of the C–H stretching peaks (2800–3000 cm^{-1}) was monitored using FT-IR (Bruker Vector 22) and plotted as a function of timed exposure to 3 mW cm^{-2} UV radiation (365 nm, black light blue lamps). The photocatalytic activity was determined by the gradient of this line.

Contact angle measurements were made using a custom-built apparatus that incorporated a digital microscope. A 100 μL droplet was applied to the surface using a syringe. The contact angle was measured using ImageJ v1.36 software. The contact angle before and after 60 min exposure to 3 mW cm^{-2} UV radiation (365 nm, BLB).

A range of nine titania (TiO_2) samples were prepared on a custom-built horizontal cold-wall atmospheric pressure chemical vapour deposition (APCVD) reactor (details have also been reported elsewhere [13,14]). The films were deposited onto SiO_2-precoated glass of dimensions 220 mm × 90 mm × 4 mm. The substrates were cleaned prior to use by washing with warm water and detergent, then rinsing with water, isopropanol and finally distilled water, before being dried in air. The substrates were heated on a graphite block containing three cartridge heaters (Watlow, 1.6 kW). All gas lines were made of stainless steel (1/4 in. o.d.) and were heated to prevent precursor condensation and ensure temperature reproducibility.

The precursors were delivered via bubblers of stainless steel construction. The bubblers were placed in aluminium jackets mounted on hotplates, so as to ensure even temperature distribution. The titanium tetraisopropoxide (Aldrich, 97%) was heated to 110 °C and added to the gas stream using pre-heated nitrogen (1.0 L min^{-1}), while the total gas flow to the reactor was 11 L min^{-1} (no additional oxygen was used). The titanium tetrachloride (Aldrich, 99.9%) was heated in the same bubbler configuration to 68 °C and was delivered to the gas stream using 0.2 L min^{-1} pre-heated nitrogen. The oxygen source for this work, ethyl acetate (Aldrich, 99.8%), was heated to 42 °C and delivered using pre-heated nitrogen. The films were grown using different conditions in order to grow a range of films that would all have varying activities and hence widen the scope of the comparative study. Film thickness was controlled using deposition time. Ethyl acetate and oxygen were used as oxidants. Two commercially available CVD grown TiO_2 coated glass samples were also investigated (Saint-Gobain, BioClean^{TM} and Pilkington, Activ^{TM}). All of the TiO_2 thin films were anatase, of different mean crystallite size (range ∼15 to >100 nm) and morphology. The conditions used to grow each sample are shown in Table 1. For samples 1–8, the precursor used was titanium tetraisopropoxide (TTIP) and for sample 9 was titanium tetrachloride ($TiCl_4$). Samples 1–4 were grown in the same conditions and vary only in thickness. Samples 5 and 6 have an additional oxygen source added to the reaction mixture, from our experience

Table 1
A summary of the conditions used to produce the TiO_2 samples

Number	Key	Deposition details	Temperature [°C]	Thickness [nm]
1	♦	TTIP	500	140
2	■	TTIP	500	110
	▲	TTIP	500	70
4	●	TTIP	500	40
5	×	TTIP + 0.2 l min^{-1} EtAc	500	40
6	+	TTIP + 0.2 l min^{-1} O_2	500	40
7	□	TTIP grown in 2% H_2 in N_2	500	40
8	△	TTIP grown in 100% H_2	500	40
9	○	$TiCl_4$ + 0.2 l min^{-1} EtAc	650	40
10	◊	BioClean^{TM}	~600	~15 nm
11	–	Activ^{TM}	~600	~25 nm

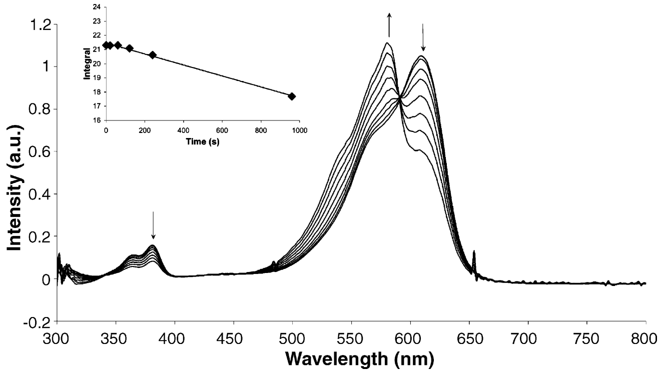

Fig. 4. A typical UV–vis spectrum showing the conversion of Rz to Rf on the surface of a BioClean^{TM} sample. The arrows indicate the direction of change. The diagram inset shows the change in integrated area as a function of exposure time to the UV lamps.

this would improve the photocatalytic activity. Samples 7 and 8 were grown in a reducing atmosphere with 2% (in N_2) and 100% H_2 used as carrier gases (in all other cases 100% N_2 was used as a carrier gas). Sample 9 was grown using a different precursor, it was again anticipated that this film would be characteristically different.

3. Results

The appearance of the ink was of a blue, slightly viscous solution. When applied (using a pipette) to the surface of the BioClean^{TM} sample the ink remained blue, showing retraction and unevenness. The uniformity of the dye was improved enormously upon placement of the microscope coverslip onto the surface. This technique of placing the microscope coverslip onto the surface was found to be highly reproducible even on surfaces were severe retraction was an issue. As shown in Fig. 3, by using this method, it was possible to produce ink films of a uniform thickness.

Upon exposure to UV radiation over a period of a few minutes the blue ink rapidly changed colour to pink, indicating conversion from Rz to Rf. Prolonged exposure to UV radiation (hours) resulted in complete destruction of the dye a with the sample appearing colourless, i.e. photobleaching.

The rate of conversion of Rz to Rf (R_{ink} units: absorbance units min^{-1}) was monitored using UV/vis spectrometry. A typical spectrum is shown in Fig. 4. To avoid any error as a result of the deconvolution of the peaks at ~580–610 nm (corresponding to the simultaneous disappearance of Rz and concurrent appearance of Rf), the smaller double peak associated only to the disappearance of Rz at 380 nm was analysed spectrophotometrically. For the measurement of the activity, the integral of the area under this peak was taken and plotted as a function of radiation time. A typical plot is shown as in inset of Fig. 4. This straight-line plot was taken as a measure of the activity of the titanium dioxide surface.

The variation in the rate of conversion of Rz to Rf (R_{ink}) was studied as a function of TiO_2 film thickness. The rate of destruction of stearic acid was also studied for these films. The two sets of results (dye test and stearic acid test) are shown and correlated in Fig. 5. It can be seen that the results correlate very well, with an almost linear relationship. Such a correlation is of particular

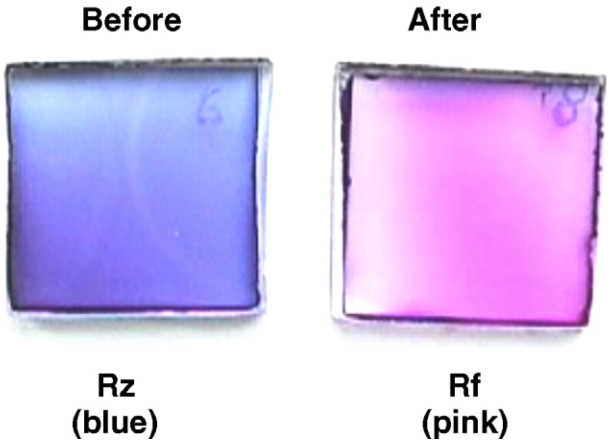

Fig. 3. A photograph of a typical dye test experiment showing the 20 mm × 20 mm sample (with coverslip), before and after ultra-bandgap radiation, the overall transmission shift can be seen.

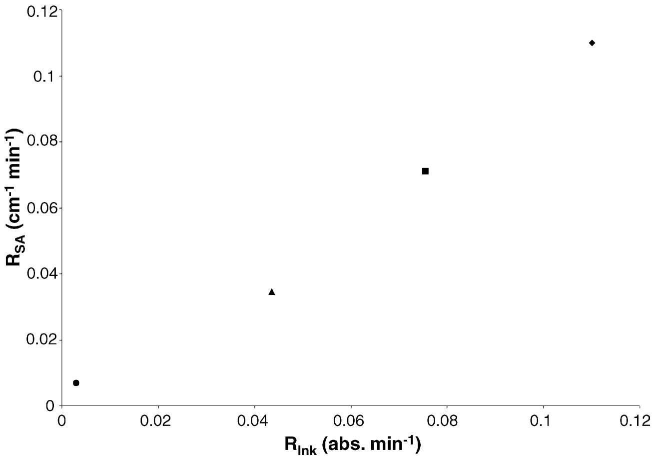

Fig. 5. Plot of rate of stearic acid removal (R_{SA}) vs. the rate of conversion of Rz to Rf (R_{ink}) for a series of TiO_2 samples of different thickness (see Table 1): (♦) sample 1 (TTIP, 140 nm), (■) sample 2 (TTIP, 110 nm), (▲) sample 3 (TTIP, 70 nm), and (●) sample 4 (TTIP, 40 nm).

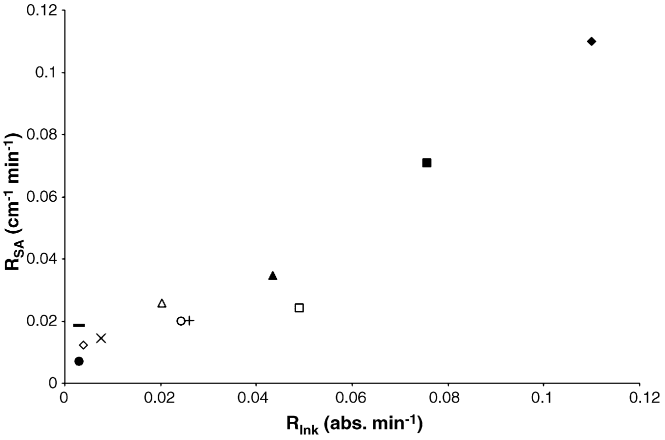

Fig. 6. Plot of rate of stearic acid removal (R_{SA}) vs. the rate of conversion of Rz to Rf for a range of TiO_2 samples (see Table 1): (♦) sample 1 (TTIP, 140 nm), (■) sample 2 (TTIP, 110 nm), (▲) sample 3 (TTIP, 70 nm), (●) sample 4 (TTIP, 40 nm), (×) sample 5 (TTIP + EtAc, 40 nm), (+) sample 6 (TTIP + O_2, 40 nm), (□) sample 7 (TTIP + 2% H_2, 40 nm), (△) sample 8 (TTIP + 100% H_2, 40 nm), (○) sample 9 ($TiCl_4$ + EtAc, 40 nm), (◇) sample 10 (BioClean^{TM}), and (–) sample 11 (Activ^{TM}).

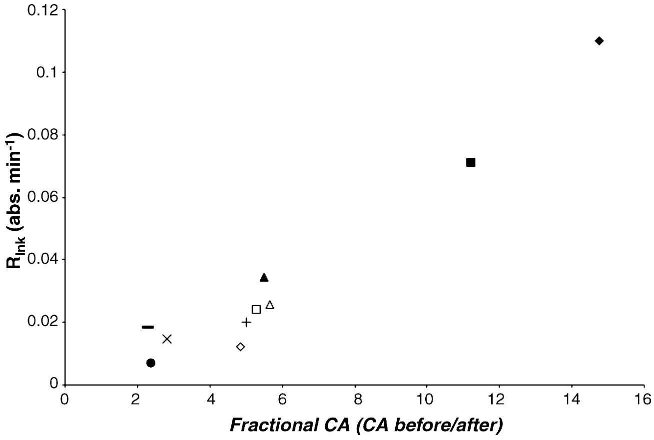

Fig. 7. Plot of rate of conversion of Rz to Rf (R_{ink}) vs. the fractional change in contact angle (CA_{before}/CA_{after}) before and after 60 min of radiation, for a range of TiO_2 samples (see Table 1): (♦) sample 1 (TTIP, 140 nm), (■) sample 2 (TTIP, 110 nm), (▲) sample 3 (TTIP, 70 nm), (●) sample 4 (TTIP, 40 nm), (×) sample 5 (TTIP + EtAc, 40 nm), (+) sample 6 (TTIP + O_2, 40 nm), (□) sample 7 (TTIP + 2% H_2, 40 nm), (△) sample 8 (TTIP + 100% H_2, 40 nm), (◇) sample 10 (BioClean^{TM}), and (–) sample 11 (Activ^{TM}). N.B.: It was not possible to measure contact angle for sample 9 due to damage in earlier tests.

importance to the acceptance of the validity of the dye test as an "in the field" method of assessment of photocatalytic activity, as the stearic acid test is generally held as the "benchmark" test for determination of photocatalytic activity. These results are also encouraging as the timescale for obtaining the dye test results was considerably quicker than that for the stearic acid test, and therefore offers advantages as a quicker quantitative laboratory based method (where a UV/vis Spectrophotometer is available) as well as being suitable for qualitative field use.

The photocatalytic activities of the CVD grown TiO_2 coatings shown in Table 1 were determined using the dye and stearic acid tests. The additional process changes were introduced (based on known experience), to significantly effect film properties, such as growth rate or crystallinity, and hence expand the scope of the study. These results were correlated and are shown in Fig. 6. It can be seen that in spite of such a range of the significantly different TiO_2 films, a reasonable correlation is still achieved. This is again encouraging in terms of validating the dye test as a quantitative method of determination of photocatalytic activity. The anomalies in the correlation shown in Fig. 6 are not surprising since the photoactivity result is influenced by both the underlying mechanisms occurring in the test as well as the film characteristics.

Contact angle measurement is another widely used indicator for photo-induced changes in thin films. It was thus decided to also correlate both dye and stearic acid activity to contact angle. All of the samples demonstrated a reduced contact angle upon exposure to UV radiation. The contact angle results were plotted as a fraction of the initial contact angle divided by the final contact angle, such interpretation allowed for easier comparison to the dye and stearic acid activity results. It should therefore be noted that a higher fractional contact angle result indicates better photocatalytic performance. In Fig. 7, the photoactivity results determined by the dye test have been correlated with those determined by a reduction in contact angle upon UV exposure. It can be seen that the correlation seems to follow a trend, indicating that films with a higher activity when determined using the dye test will concurrently show a greater reduction in contact angle upon exposure to UV radiation.

Another interesting comparison is shown in Fig. 8—between the stearic acid test and contact angle results. These results show another useful correlation and equally suggested that photocatalytic activity of the films when determined by the stearic acid test is directly related to the contact angle performance. The results in both Figs. 7 and 8 provide some very valid and interesting evidence to support of the explanation of the mechanism behind photo-induced superhydrophilicity (PSH) that is

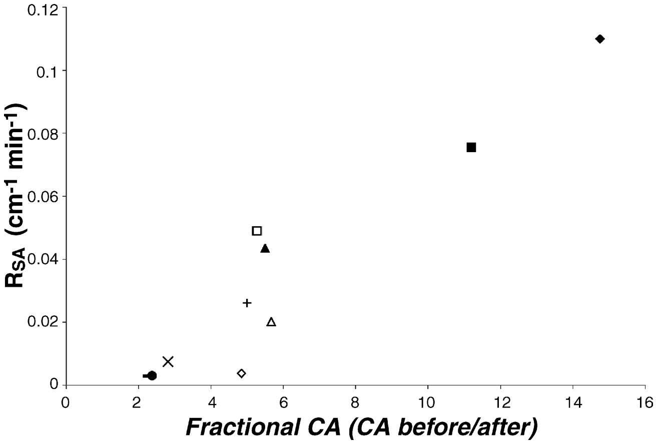

Fig. 8. Plot of rate of stearic acid removal (R_{SA}) vs. the fractional change in contact angle (CA_{before}/CA_{after}) before and after 60 min of radiation, for a range of TiO_2 samples (see Table 1): (♦) sample 1 (TTIP, 140 nm), (■) sample 2 (TTIP, 110 nm), (▲) sample 3 (TTIP, 70 nm), (●) sample 4 (TTIP, 40 nm), (×) sample 5 (TTIP + EtAc, 40 nm), (+) sample 6 (TTIP + O_2, 40 nm), (□) sample 7 (TTIP + 2% H_2, 40 nm), (△) sample 8 (TTIP + 100% H_2, 40 nm), (◇) sample 10 (BioClean^{TM}), and (–) sample 11 (Activ^{TM}). N.B.: It was not possible to measure contact angle for sample 9 due to damage in earlier tests.

observed on the surface of TiO_2 thin films. Two explanations have been proposed and literature exists to support both. One proposal is that under ultra-bandgap radiation the TiO_2 photogenerated electrons tend to reduce the Ti(IV) cations to Ti(III), and the holes oxidise the O^{2-} anions. In the process, oxygen atoms are ejected, creating oxygen vacancies, water molecules can then occupy these vacancies creating OH-groups, which tend to make the surface hydrophilic [15,16]. However, the other proposal – which is the proposal supported by the evidence herein – relates PSH more to the ability of the material to photo-mineralise surface organics, resulting in a "clean" surface and hence enhanced wetability [17,18], therefore agreeing with the observations presented here in which the ability of the surface to photo-mineralise an organic pollutant (i.e. either dye or stearic acid) is directly related to its ability to show PSH upon ultra-bandgap radiation.

4. Conclusions

The results show that a film based dye test is an encouragingly quick and qualitative method for the determination of the photoactivity of thin films of TiO_2. The potentially "simple-to-use" test, the clear visible change, and the short timescale involved, give the dye test significant advantages over conventional photoactivity tests.

The comparison of photoactivity when determined using the dye and stearic acid tests indicates an encouraging correlation between the two tests. For similar films of different thickness the correlation was reasonably linear. Where a range of different growth parameters were investigated correlation was more complex. The most probable reason for this is the very different growth parameters used to grow the different samples, these would obviously result in different surface chemistries, morphology, crystallinity and composition, and therefore consequentially lead to different dye and stearic acid activity correlation. The direct correlation with contact angle, which has not been reported before, encouragingly supports general correlation between all three tests, It is interesting to note that whilst good linearity within any one photoactivity test can be demonstrated, the correlation between tests is less good. This result shows the complexity of the differing processes involved. The results also showed evidence in support of literature observations that the mechanism that gives rise to PSH is intimately related to that of photo-mineralisation.

The above general conclusion must be tempered with the knowledge that the results illustrated in Figs. 6–8 is for a limited data set and weighted for the results for the four titania thin films of different thickness synthesised under the same conditions. More work is required to fully establish the relationships described above and the influence of other factors, such as surface morphology and crystal phase, on photocatalytic activity.

The dye-based test has value not only to speed up laboratory investigations, but interesting potential for use "in-the-field", i.e. to demonstrate to consumers, and to check and then retest, and importantly verify photoactivity in situ—a capability which is currently not available.

Acknowledgement

The authors gratefully acknowledge the support of the EC (project: GRD1-2001-40791).

References

[1] A. Mills, S.K. Lee, J. Photochem. Photobiol. A: Chem. 152 (2002) 233–247, and references therein.

[2] http://www.pilkington.com.

[3] http://www.selfcleaningglass.com.

[4] http://www.suncleanglass.com.

[5] K.D. Sanderson, A. Mills, I.P. Parkin, S. Hurst, A. Lepre, I. McKittrick, D. Rimmer, L. Ye, S.A. O'Neill, Soc. Vac. Coaters 46th Annual Technical Conference Proceedings, 2003, pp. 203–208.

[6] A. Mills, S. Lee, A. Lepre, I.P. Parkin, S.A. O'Neill, Photochem. Photobiol. Sci. 1 (11) (2002) 865–868.

[7] J. Shang, W. Li, Y. Zhu, J. Mol. Catal. A: Chem. 202 (2003) 187–195.

[8] A. Mills, N. Elliott, I.P. Parkin, S.A. O'Neill, R.J. Clark, J. Photochem. Photobiol. A: Chem. 151 (2002) 171–179.

[9] http://www.cost540.com/, accessed November 2006.

[10] http://www.iso.org/iso/en/CatalogueListPage.CatalogueList?COMMID=4580&scopelist=PROGRAMME, accessed November 2006.

[11] A.J. Julson, D.F. Ollis, Appl. Catal. B: Environ. 65 (2006) 315–325.

[12] A. Mills, M. McGrady, J. Wang, J. Phys. Chem. B 110 (2006) 18324–18331.

[13] P. Evans, The growth of photocatalytically active TiO_2 thin films on stainless steels using atmospheric pressure chemical vapour deposition (APCVD), Ph.D. Thesis, University of Salford, September 2005.

[14] P. Evans, M.E. Pemble, D.W. Sheel, Chem. Mater. 18 (2006) 5750–5755.

[15] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C: Rev. 1 (2000) 1–21.

[16] T. Watanabe, A. Nakajima, R. Wang, M. Minabe, S. Koizumi, A. Fujishima, K. Hashimoto, Thin Solid Films 351 (1999) 260–263.

[17] J.M. White, J. Szanyi, M.A. Henderson, J. Phys. Chem. B 107 (2003) 9029–9033.

[18] T. Zubkov, D. Stahl, T.L. Thompson, D. Panayotov, O. Diwald, J.T. Yates, J. Phys. Chem. B 109 (2005) 15454–15462.